Synthesis of hyperbranched polybenzoxazoles and their molecular composites with epoxy resins

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ABSTRACT: Hyperbranched aromatic polymers have attracted great attention recently because they combined the processability of hyperbranched polymers and the high-level performance of aromatic polymers. Here, a one-pot strategy for the synthesis of hyperbranched Polybenzoxazoles (HBPBOs) by polycondensation of 2,2-Bis (3-amino-4-hydroxyphenyl) hexafluoropropane and 1,3,5-benzenetricarboxylic acid in Polyphosphoric acid was reported. The HBPBOs exhibited good solubility in organic solvents because of the branched structure and the flexible hexafluoropropane groups in main chains. The structure and terminal functional groups could be tailored by adjusting the molar ratio of two monomers. FT-IR, NMR and XRD measurements confirmed the structure of HBPBOs, while thermogravimetric analysis (TGA), UV-vis, and photoluminescence spectra, combined with the comparison with linear PBOs demonstrated the intriguing optical properties and good thermal stabilities of HBPBOs. The good solubility of HBPBOs also permitted their usage as molecular reinforcement for polymer composites as demonstrated in this study of HBPBOs/epoxy composites. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41942.

INTRODUCTION

Aromatic heterocyclic polymers, such as polyimide (PI), polybenzimidazole (PBI), Polybenzoxazole (PBO), and polybenzothiazoles (PBT), have been extensively investigated in both scientific and industrial communities because of their exceptional properties that could not attain from traditional polymers, such as excellent mechanical, thermal, and electrical properties, which make them promising candidates in diverse applications of aerospace, firefighting, microelectronics, fuel cells, and so on.[1–4] Among these polymers, PBO possesses the highest thermal stability with decomposition temperature up to 650°C because of its ladder-like rigid polymer chains.[5] PBO fibers, which were spun from the liquid crystal solution of PBO in polyphosphoric acid, show the highest Young's modulus of 270 GPa among commercially available polymers.[6] Such outstanding properties make PBO stand out among other high-performance polymers for next-generation extreme materials. As a conjugated polymer, PBO also exhibits interesting optical properties. Han's group and others have extensively investigated the photophysical properties of PBO and its copolymers, and demonstrated their promising applications in photoelectronic devices.[7–9]

It is the rigid-rod polymer chains that endow PBO with these super properties, however, it inevitably makes PBO incompliant with common processing, because PBO can neither be dissolved in common solvents nor melt before decomposition.[10,11] Although PBO can be processed in some strong acid, such as polyphosphoric acid and methanesulfonic acid, Han *et al.* have demonstrated the formation of aggregates of PBO chains in such acid, which were harmful to their optical properties.[7] Moreover, despite it is recognized that PBO is an ideal reinforcing agent for polymer composites, the insoluble feature of PBO makes it only possible to reinforce polymer matrix in the form of fibers, while unable to directly incorporate the rigid-rod chains into polymers on molecular level.[2,6] As a result, efforts have been taken to make soluble PBO, but it is usually a challenging task. For example, it is shown that the incorporation of fluorine atoms in aromatic polymers, such as PI, could improve its solubility,[12] while the fluorinated PBO was not always soluble in organic solvent,[13] which may be because of the higher interchain packing ability of benzoxazole groups as compared to imide rings, flexible bonds were further needed to reduce the chain rigidity.[14,15] Partial replacement of aromatic rings with aliphatic moieties represents another method to improve the

solubility of aromatic polymers, but the thermal stabilities are inevitably deteriorated.[16,17]

The introduction of hyperbranched structure constitutes another facilitate approach to tailor the physicochemical properties of linear polymers. Hyperbranched polymers (HBPs) are a special class of dendritic polymer, but unlike perfect dendrimers, HBPs can be synthesized via one-step polymerization, which offers great promising for large-scale preparation.[18–20] Owing to their globular and porous structure, HBPs generally exhibit better solubility and processibility than their linear counterparts because such configuration could lower the entanglement or packing of polymer chains. The lowered intermolecular interaction also offers possibility to tune the electronic properties, transporting properties, and optical properties of HBPs. One major application of HBPs of commercial interest is the use as polymer additive, because the globular configuration of HBPs is expected to modify the rheological property of matrix polymer.[18] Additionally, the high level end-group functionality in HBPs could improve the compatibility or reactivity to polymer matrix, and the branched structure in HBPs could further provide mechanical interlocking to other polymers.[21]

Given the merits of HBPs, numerous hyperbranched aromatic polymers, such as hyperbranched PBI,[22] PBT,[23] PI,[24] poly(arylene ether)s,[25] and poly(ether ketone)[26] have been synthesized with the aim of improving their processibility and exploiting new functionalities. However, only a few papers on hyperbrached PBO (HBPBO) have been published.[27–29] For instance, Kudo *et al.* synthesized HBPBOs in two steps via the thermal cyclodehydration of a hyperbranched poly(o-hydroxyamide), which was preprepared by A_2+B_3 strategy.[27] Unfortunately, the HBPBOs were still not soluble in common organic solvents. Baek's group has reported the synthesis of HBPBO via the polycondensation of specially designed AB_2 monomers and the subsequent modification of HBPBO by its peripheral functional groups. The HBPBOs or modified HBPBOs thus obtained were soluble in most of polar aprotic solvents.[28,29] However, the synthesis of AB_2 monomers generally involves multistep reaction sequences.

Herein, we report for the first time the synthesis of soluble HBPBOs by one-pot direct polycondensation of commercial available A_2 and B_3 monomers in polyphosphoric acid. The introduction of fluorine atoms in the branched backbone of HBPBOs was found to be crucial for their solubility in organic solvents. The peripheral functionalities of HBPBOs could be readily adjusted by simply changing the molar ratio of A_2 and B_3 monomers. The physicochemical properties of HBPBOs were thoroughly characterized and compared to their linear counterpart. As a result of the good solubility of our HBPBOs in common organic solvents, HBPBOs reinforced epoxy composites on the molecular level were fabricated and the effect of HBPBOs on the properties of epoxy was evaluated. It is found that the surface wettability of epoxy can be tailored by incorporating small amount of different HBPBOs, and the thermal stabilities of all composites are superior to that of neat epoxy resins.

EXPERIMENTAL

Materials

2,2-Bis (3-amino-4-hydroxyphenyl) hexafluoropropane (6FAP), 3,3-Dihydroxy-4,4'-diaminobiphenyl (HAB), 1,3,5-benzenetricarboxylic acid (BTA), and terephthalic acid (TPA) were purchased from Shanghai Bangcheng Chemical. Polyphosphoric acid (PPA), phosphorus pentoxide (P_2O_5), Methanesulfonic acid (MSA), concentrated sulfuric acid (H_2SO_4), and all organic solvents were obtained from Sinopharm Chemical Reagent (SCRC). Sodium hydrocarbonate ($NaHCO_3$) were purchased from shanghai Titanchem. Epoxy resin of commercial grade, Epon44 was got from Jin Hong. 4,4'-Methylenedianiline (MDA) was purchased from J&K Chemical in Shanghai. All reagents and solvents were used as received without purification.

Synthesis of HBPBOs

In a typical synthesis of HBPBOs, certain amount of 6FAP was added into 86 g of PPA containing 85 wt % P_2O_5 with stirring under nitrogen flow. After the 6FAP was dissolved in PPA completely, BTA with different molar ratios to 6FAP was slowly added. The mixture was then mechanically stirred under nitrogen flow at 150°C for 4 h and 190°C for 20 h. As the reaction processed, the mixture turned deep red-brown and became very viscous. After cooling to room temperature, the reaction mixture was poured into deionized water. The resulting precipitates were then neutralized with the solution of $NaHCO_3$ and filtered. The solids were further washed with water for several times. Finally, the solid was filtered off and dried in vacuo at 80°C for 24 h.

Fabrication of HBPBOs/Epoxy Composites

In the fabrication of HBPBOs/Epoxy composites, epoxy resin (2 g) was added in 10 mL of DMF solution containing 24.3 mg of HBPBOs. The solution was stirred until homogeneous and then the DMF was removed with a rotary evaporator. After that, 0.406 g of MDA was added and homogeneously mixed with epoxy to afford a curable mixture. The content of HBPBOs in composites was thus 1 wt %. The final mixture was poured into a dog-bone shaped mould and degassed in vacuum oven for approximately 60 min, followed by a post cure at 80°C for 2 h, then 120°C for 2 h, and finally 150°C for 2 h.

Characterizations

The inherent viscosities of HBPBOs were measured by an Ubbelohde viscometer in MSA at 30°C with concentrations of 0.5 g/dL. The choice of MSA as solvent to perform intrinsic viscosity measurement was based on its good solubility to PBOs and the much lower viscosity of polymer solution as compared to that of polymers in PPA/P_2O_5 solvent. The FT-IR spectra were recorded on a NICOLET 6700 FT-IR instrument (Thermoscientific, USA). The ^1H NMR spectra of HBPBOs were recorded on Avance 400 NMR spectrometer (Bruker, switzerland) in DMSO-d_6. The XRD patterns were measured with D/max-2550 PC X-ray powder diffraction instrument (Rigaku, Japan). Thermogravimetric analysis (TGA) was carried out using a Netzsch TGA 209 F1 instrument under nitrogen atmosphere at a heating rate of 10°C/min. The UV-vis spectra of polymers in MSA and NMP were obtained by Lambda 35 UV-Vis spectroscopy instrument (Perkin Elmer, USA). The photoluminescence spectra were

recorded on a LS55 fluorescence spectrophotometer at room temperature. Contact angles of water on surfaces of composites were obtained from OCA40Micro Automatic video micro contact Angle measurement instrument. The tensile properties of composites were measured at room temperature using a WDW3020 instrument at a crosshead speed of 5 mm/min with humidity about 50%, the initial gauge length was 30 mm, at least four specimens were tested for each samples for accuracy.

RESULTS AND DISCUSSION

Synthesis and Characterization of HBPBOs

Two approaches were generally employed to synthesize aromatic HBPs, one is the self-polymerization of an AB_x (where $X \geq 2$) monomer, the other is the polymerization of a difunctional A_2 monomer and a trifunctional B_3 monomer. In contrast to the tedious process for the synthesis of AB_x monomer in the first approach, the $A_2 + B_3$ strategy takes advantages of commercially available and cost-effective monomers, and the possible mass production. Therefore, $A_2 + B_3$ approach was selected in this study for the synthesis of HBPBOs, commercially available compounds, 6FAP and BTA, were used as A_2 and B_3 monomers, respectively. According to Carother's and Flory's equations,[21] it is required strictly controlled reaction conditions to avoid gelation during reaction. Therefore, several ways were adopted to prevent gelation in this study: (1) BTA was slowly added in the reaction mixture; (2) adjusting the molar ratio of 6FAP and BTA to break the stoichiometrical balance between o-aminophenol and carboxyl functionalities; (3) controlling the total monomer concentrations in the reaction systems. In addition, the excess of 6FAP or BTA would generate HBPBOs with different terminal groups, which could result in different structure or properties. Therefore, we have adjusted the molar ratio of 6FAP and BTA to 1 : 1 (there were excess of carboxyl groups), 3 : 2 (the carboxyl and o-aminophenol groups were equivalent), and 9 : 4 (there were excess of o-aminophenol groups), which would produce carboxyl-terminated HBPBO (HBPBO-1), HBPBO with equivalent carboxyl and o-aminophenol end groups (HBPBO-2), and o-aminophenol-terminated HBPBO (HBPBO-3), as shown in Figure 1.

With these recipes in mind, we first tried to find the optimal monomer concentrations for the synthesis of HBPBOs, as high concentration would lead to gelation while low concentration would result in low molecular weight. It is found that the critical monomer concentrations (CMCs) of HBPBO-1, HBPBO-2, and HBPBO-3 in reaction solvent of PPA/P₂O₅ during synthesis reaction were about 4, 2, and 4 wt %, respectively. Homogenous polymer solution without gelation could be obtained when the monomer concentration below the CMC. The lower CMC of HBPBO-2 indicates that this reaction system gelated more easily because the equivalent amount of A_2 and B_3 monomers could form cross-linked network more easily and completely than monomers with non-stoichiometrical feed ratios. The intrinsic viscosity (η) of HBPBOs at the corresponding CMCs were measured to be 0.80, 1.33, and 0.34 dL/g, respectively, which was consistent with the expectation that equivalent amount of A_2 and B_3 monomers would result in polymers with higher molecular weight. It is noteworthy that although the CMCs and
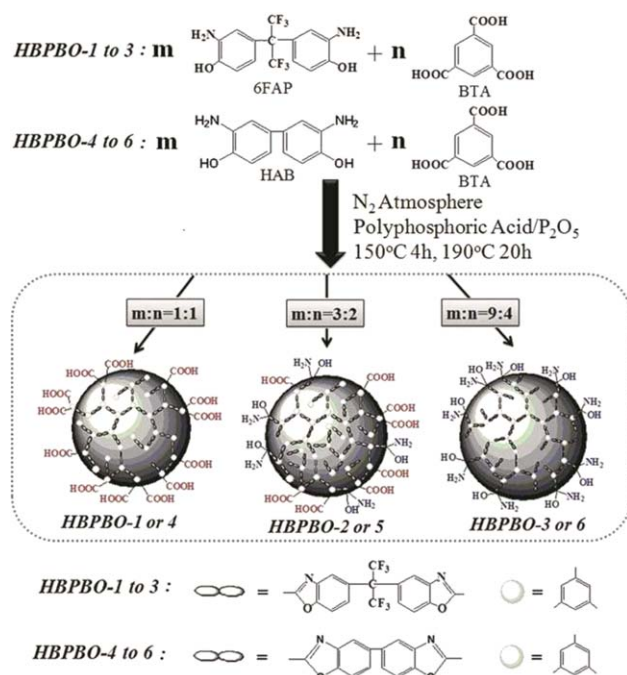

Figure 1. Synthesis of HBPBOs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the excess amount of one functional group over the other one were identical for HBPBO-1 (50% excess of carboxyl groups) and HBPBO-3 (50% excess of o-aminophenol groups), the η of HBPBO-1 was much higher than HBPBO-3. This may be because of the fact that as the trifunctional monomers were excess in HBPBO-1, not all carboxyl were reacted with o-aminophenol groups, when two carboxyl groups in one BTA molecule were polymerized but the other one was not, the BTA was actually acted as a bifunctional molecule in this case, which could increase the molecular weight of the linear units, and compromise the unbalance between carboxyl and o-aminophenol groups, thus resulted in higher η of HBPBO-1. The monomer concentration of synthesis reaction was also found to influence the molecular weight of HBPBOs with the same molar ratio of monomers, for example, the η of HBPBO-1 polymerized at 2 and 3 wt % monomer concentrations were 0.28 and 0.43 dL/g, underlining the importance of synthesizing HBPBOs at their corresponding CMCs.

The solubility of HBPBOs was then tested, as shown in Table I. Besides the generally used strong acid for dissolving PBO, such as MSA, PPA, and H₂SO₄, the HBPBOs were also soluble in most of the polar aprotic solvents such as N-methyl-2-pyrrolidinone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) at room temperature or elevated temperatures, and even partially soluble in less powerful solvents such as tetrahydrofuran (THF) and chloroform regardless of the terminal groups or molecular weight, demonstrating the good solubility of our HBPBOs.

The branched structure and the presence of hexafluoropropane groups in the backbones were thought to be responsible for the good solubility of HBPBOs. To confirm this hypothesis, two

Table I. The Critical Monomer Concentrations, inherent Viscosities and Solubility of HBPBOs in Various Solvents

Sample	Critical monomer concentration (wt %)	η (dL/g)	Solubility[a]								
			MSA	PPA	H_2SO_4	NMP	DMAc	DMF	DMSO	THF	$CHCl_3$
FPBO	–	1.80	+++	++	+++	+	−	−	+	−	−
HBPBO-1	4	0.80	+++	+++	+++	+++	++	++	++	++	+
HBPBO-2	2	1.33	+++	++	+++	+++	++	++	+	+	+
HBPBO-3	4	0.34	+++	+++	+++	+++	++	++	++	+	+
HBPBO-4	2	0.29	+++	++	+++	+	+	+	+	−	−
HBPBO-5	1	1.15	+++	++	+++	−	−	−	−	−	−
HBPBO-6	1	0.44	+++	++	+++	+	−	−	−	−	−

[a] +++, soluble at room temperature; ++, soluble upon heating; +, partially soluble upon heating; −, insoluble. The concentrations of polymers in solvents were 5 mg/mL.

sets of control experiments were carried out. On one hand, we prepared linear fluorinated PBO (FPBO) by polymerization of TPA and BTA at 4 wt % monomer concentration. The FPBO showed higher η of 1.80 dL/g than HBPBOs, which might be resulted from the higher molecular weight or chain entanglements than HBPBOs. However, FPBO could only be dissolved in strong acid and partially dissolved in NMP and DMSO (Table I), demonstrating the important roles of branched structure and end-groups in determining the solubility of HBPBOs. On the other hand, we also prepared a series of HBPBOs without hexafluoropropane groups in the backbone by polymerization of HAB and BTA (Scheme 1, HBPBO-4 to 6, in which the molar ratio of HAB and BTA were adjusted to 1 : 1, 3 : 2, and 9 : 4, respectively). It was found that the rigid monomer HAB greatly influenced the polymerization behavior of HBPBOs. For example, the CMCs of HBPBO-4, HBPBO-5, and HBPBO-6 were determined to be 2, 1, and 1 wt %, respectively, much lower than corresponding HBPBO-1, HBPBO-2, and HBPBO-3. The η of HBPBO-4, HBPBO-5, and HBPBO-6 were found to be 0.39, 1.15, and 0.44 dL/g, which were also lower than their fluorinated counterparts. These phenomena suggested the rigid polymer chains facilitated the formation of gel network, thus hampered the synthesis of HBPBOs with high molecular weight. The solubility of HBPBOs without hexafluoropropane groups were also inferior to fluorinated HBPBOs, as listed in Table I. These HBPBOs were only soluble in strong acid but could not be dissolved in common organic solvents. These comparisons demonstrated our hypothesis that both the structure and composition contributed to the solubility of our fluorinated HBPBOs. As our goal was synthesis of soluble HBPBOs, therefore, in the following sections, only HBPBO-1, HBPBO-2, and HBPBO-3 were characterized and compared to their linear counterpart.

The structures of HBPBOs were characterized by FTIR and ^{1}H NMR. The FTIR spectra of HBPBOs are shown in Figure 2. All HBPBOs exhibited strong absorption peak at 1134 and 1249 cm^{-1}, which can be assigned to the multiple stretching of C-F bonds. The characteristic peaks at 1625 cm^{-1}, which was attributed to the characteristic C=N stretching of benzoxazole rings,[30] could also be found in all HBPBOs. For HBPBO-1,

there was a strong peak at about 1720 cm^{-1}, indicating the presence of carboxyl groups, which was in agreement with the structure model (Scheme 1) of HBPBO-1. However, although the carboxyl groups should also be presented in HBPBO-2, the peak at 1720 cm^{-1} was not distinguishable in the spectrum because of the much less amount of carboxyl in HBPBO-2. In HBPBO-3, the peak intensity at 3430 cm^{-1} was much stronger, indicating more peripheral –OH and -NH$_2$ groups were existed than those in HBPBO-2 because of its lower molecular weight.

Figure 3 shows the ^{1}H NMR spectra of HBPBOs. However, because of the relatively poor solubility of HBPBO-2 in DMSO, the spectrum of HBPBO-2 displayed only fused broad peak but not well-resolved peaks. For HBPBO-1 and HBPBO-3, the possible existed moieties, that is, the dendritic units, the linear units, and the terminal units were also exemplified in Figure 2. The resonances observed at 8.90–9.14 ppm in HBPBO-1 and HBPBO-3 can be attributed to the dendritic BTA moiety.[31] The resonances at about 7.30–8.10 ppm were assigned to the linear bibenzoxazole units. For HBPBO-1, the peaks of terminal BTA units can be found at 8.66 ppm, and small peaks for linear disubstituted BTA was at about 7.07 and 8.80 ppm. While the
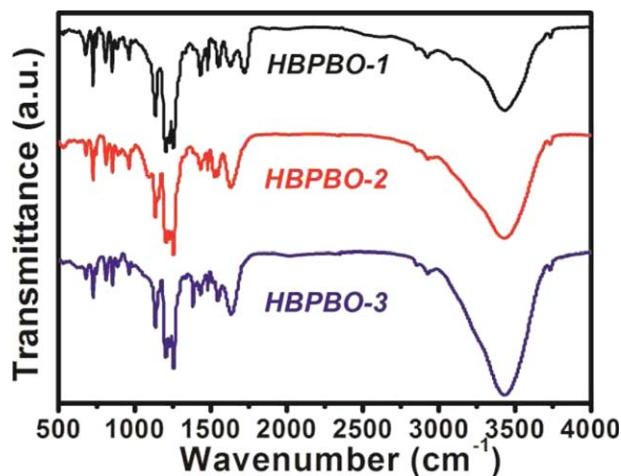

Figure 2. FT-IR spectra of HBPBOs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
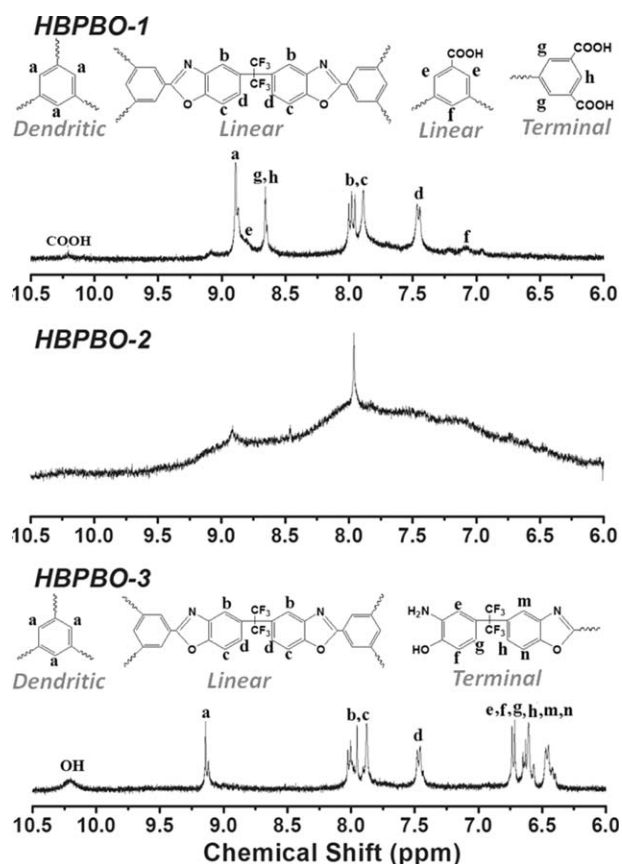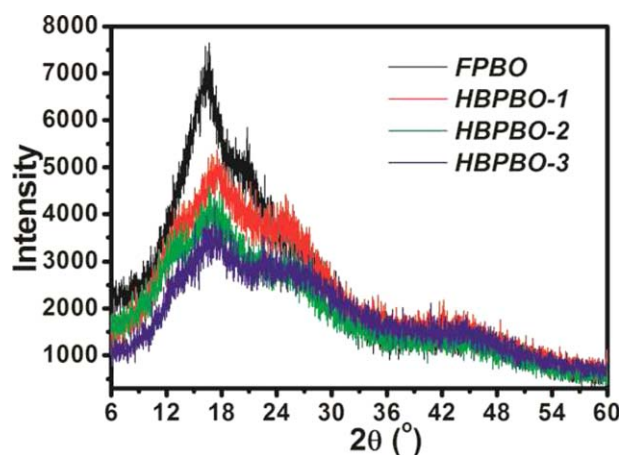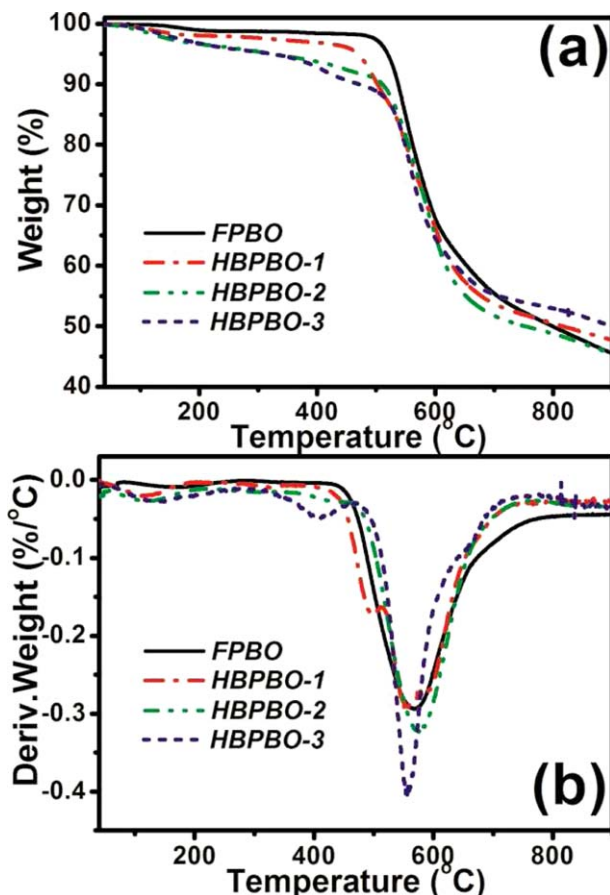
Figure 3. ^{1}H NMR spectra of HBPBOs.

Figure 5. TGA and DTG curves of FPBO and HBPBOs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resonances of terminal 6FAP units in HBPBO-3 were at about 6.38–6.78 ppm. The degree of branching (DB) can be calculated by the Fréchet definition.[32] $DB = (D + T)/(D + T + L)$, where D, T, and L correspond to the number of dendritic, terminal, and linear units in the polymer. Thus, the DB for HBPBO-1 and HBPBO-3 were 0.45 and 0.58, respectively. The lower DB of HBPBO-1 was consistent with our hypothesis that a part of BTA would act as difunctional monomers, which resulted in increased numbers of linear units.

Figure 4. XRD patterns of FPBO and HBPBOs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To probe the packing structure of the polymer chains, XRD measurements were conducted on HBPBOs and compared to that of FPBO, as shown in Figure 4. The characteristic diffraction peak of FPBO appeared at about 16.4°, corresponding to d-spacing of 0.54 nm, which was assigned to the side-by-side interchain ordered packing.[14,15] However, the typical peak corresponding to face-to-face packing of PBO chains at about 26°, was very weak in our FPBO, suggesting the introduction of bulk hexafluoropropane could disrupt the tight packing of benzoxazole rings. HBPBOs also showed the diffraction peaks at about 16.6–17.4°, but the shapes of these peaks become broaden, and the intensities were weakened, indicating the branched structures induced steric hindrance between polymer chains and hampered the close packing, which were contributed to the better solubility of HBPBOs.[23]

The thermal stabilities of HBPBOs were tested by TGA. The TGA and derivative thermogravimetry (DTG) curves of FPBO and HBPBOs are shown in Figure 5. The FPBO showed good thermal stability with the maximum decomposition temperature (T_d) at about 567.6°C. While for HBPBOs, there was gradual weight loss below 500°C, which were attributed to the degradation of peripheral functional groups. However, the T_d of HBPBOs seemed not deteriorating too much. The T_d for HBPBO-1, HBPBO-2, and HBPBO-3 was about 558.8°C,
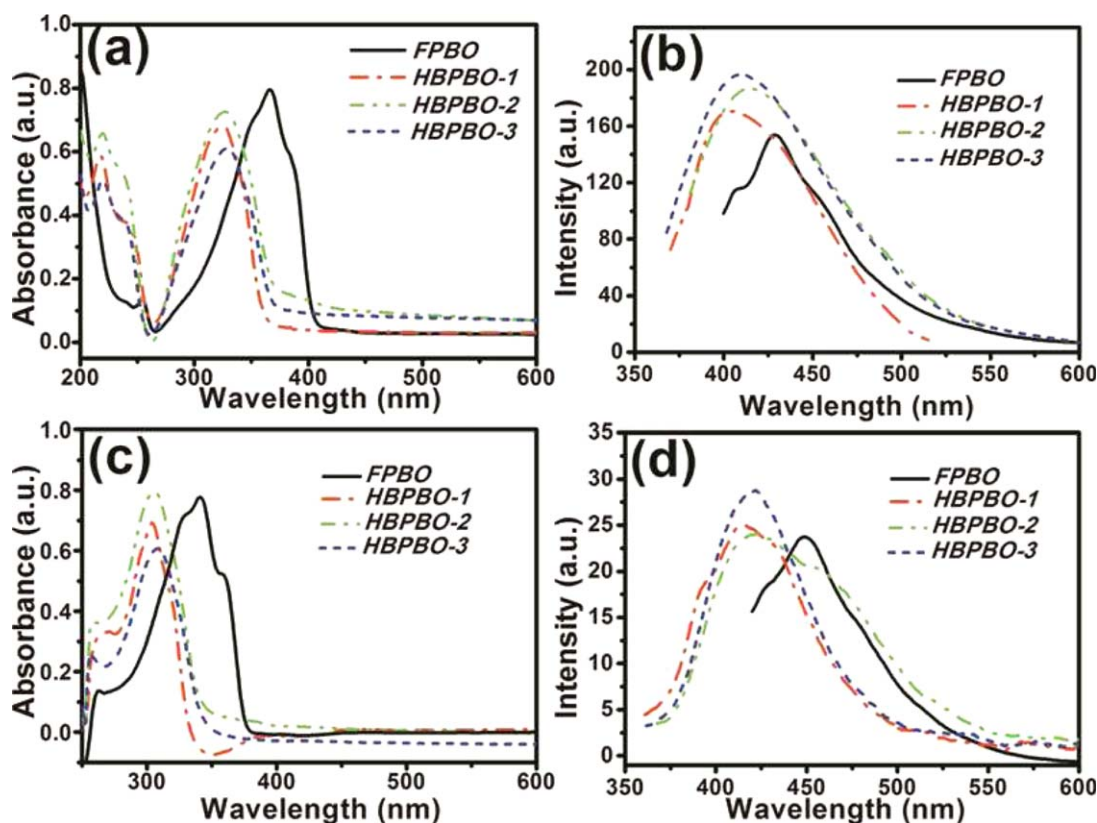
Figure 6. The UV-vis spectra of polymers in (a) MSA and (c) NMP, and the fluorescence emission spectra of polymers in (b) MSA and (d) NMP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

556.4°C, and 573.4°C, respectively, demonstrating that HBPBOs also have good thermal stabilities. The higher thermal stability of HBPBO-2 as compared to HBPBO-1 and HBPBO-3 was in accordance with the intrinsic viscosity of HBPBOs.

The optical properties of HBPBOs were measured by UV-vis and photoluminescence spectroscopies in both MSA and organic solvent NMP, as shown in Figure 6. In MSA [Figure 6(a)], the maximum absorption peak (λ_{max}) for FPBO was appeared at 365 nm, corresponding to the π-conjugated structure of benzoxazole moieties in linear FPBO. However, the λ_{max} of HBPBO-1, HBPBO-2, and HBPBO-3 blue-shift to 324, 326, and 330 nm, respectively, indicating the coplanarity of rigid chains has been distorted by the kinked structure of HBPBOs.[23,33] The introduction of branched structure has also shortened the conjugated length, the combined effect the above resulted the large blue-shift of absorption peaks. Moreover, there were addition peaks at about 217–240 nm in HBPBOs, which we attributed to the characteristic peaks of functional benzoic acid, aniline, or phenol groups at periphery. The fluorescence emission spectra of polymers in MSA [Figure 6(b)] were obtained by exciting the polymer solutions at their optimized excitation wavelength. The FPBO and HBPBOs all emitted blue light from the emission spectra. Similar to absorption spectra, the emission peaks of HBPBOs were blue shifted. The emission peaks of HBPBO-1, HBPBO-2, and HBPBO-3 shifted from 429 nm to 397, 414, and 410 nm, respectively.

The absorption and fluorescence spectra of polymers in NMP are presented in Figure 6(c,d). From absorption spectra, the λ_{max} of FPBO was centered at 341 nm, while the λ_{max} of HBPBO-1, HBPBO-2, and HBPBO-3 blue shifted to 304, 305 and 308 nm, respectively, which were consistent with the optical behaviors in MSA. Note that the λ_{max} of FPBO and HBPBOs in NMP was ∼20 nm blue shifted as compared to those in MSA, this might be because of the ionic interactions of protonated benzoxazole groups in MSA, which enlarged the effective conjugation length at the ground state of HBPBOs, such phenomena was also observed by Baek *et al.*[28] In NMP, FPBO also emitted blue light at maximum wavelength of 447 nm. The peaks of HBPBO-1, HBPBO-2, and HBPBO-3 shifted to shorter wavelength of 414, 421, and 422 nm, respectively. Such results also demonstrated the advantages of branched structure in preventing the polymer chains from aggregation, which was detrimental to their usage in optical devices.

Synthesis and Properties of HBPBOs/Epoxy Composites

As HBPBOs were soluble in common organic solvents, it is possible to use HBPBOs as molecular reinforcements for traditional polymers, which could not be achieved by using linear PBOs. Epoxy resins were selected as model polymer matrix because of their good intrinsic properties and wide applications. The peripheral functionalities of HBPBOs could also ensure the strong interactions with epoxy resins. Epoxy composites with the addition of 1 wt % HBPBOs were fabricated, as shown in Figure 7. The composites were transparent with slightly
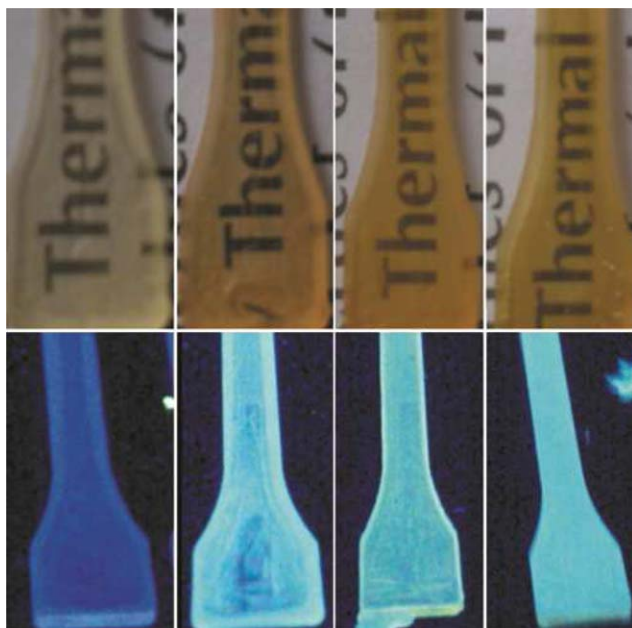
Figure 7. Photographs of epoxy and HBPBOs/Epoxy composites under natural light and UV lamp (365nm). (From left to right: epoxy, HBPBO-1/Epoxy, HBPBO-2/Epoxy, and HBPBO-3/Epoxy.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
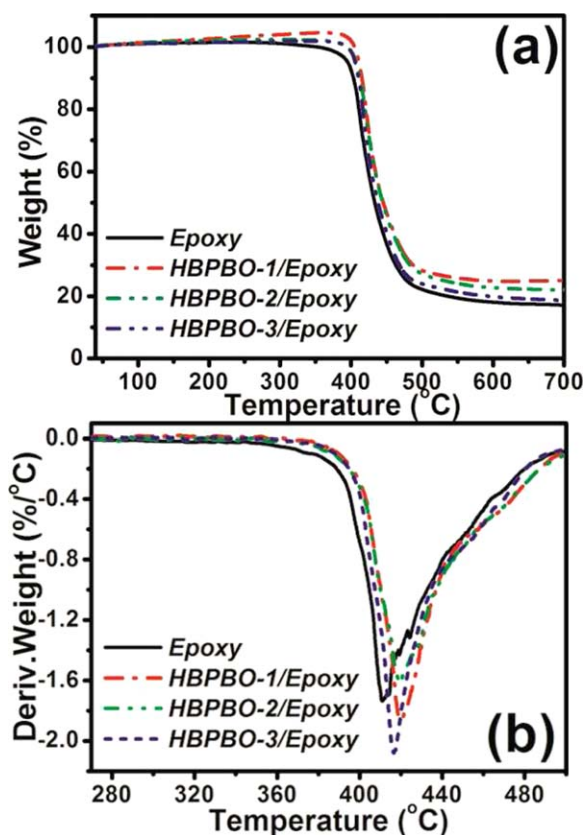

Figure 9. Contact angles of water on surfaces of epoxy and HBPBOs/Epoxy composites.

Figure 8. TGA and DTG curves of epoxy and HBPBOs/Epoxy composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
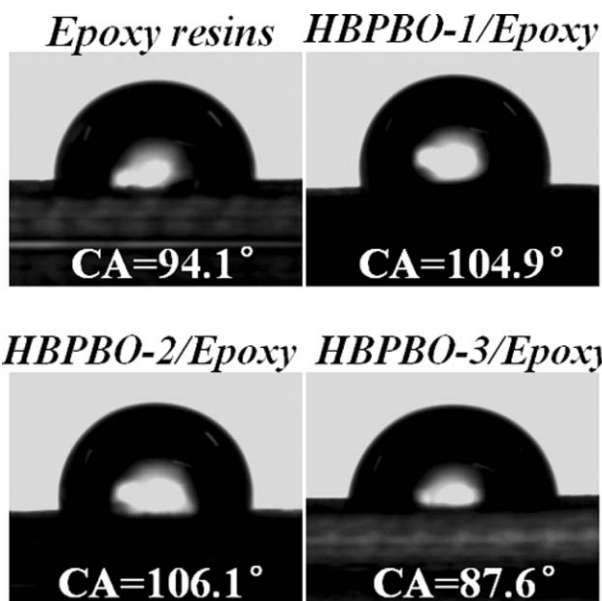
yellowish color as compared to neat epoxy. Interestingly, the composites emitted blue light under UV lamp (365 nm), which was in consistent with the fluorescence properties of HBPBOs. The emitted blue light was homogenous, suggesting the good distribution and dispersion state of HBPBOs in epoxy resins.

As HBPBOs demonstrated good thermal stabilities, we first investigated if the incorporation of HBPBOs could improve the thermal properties of epoxy. From the TGA and DTG curves of epoxy and its composites (Figure 8), it can be seen that the temperatures for 5% weight loss (T_5) of epoxy was about 395.5°C, while it increased to 411.1°C, 407.2°C, and 405.8°C upon the addition of only 1 wt % HBPBO-1, HBPBO-2, and HBPBO-3, respectively. The temperatures for maximum weight loss (T_d) were also improved from 411.0°C of epoxy to 420.2°C, 419.5°C, and 416.7°C of HBPBO-1/Epoxy, HBPBO-2/Epoxy, and HBPBO-3/Epoxy, respectively, demonstrating the positive effect of HBPBOs on the thermal stabilities of epoxy, which might be because of the lower decomposition rate of epoxy caused by interactions between epoxy and HBPBOs.[33,34] The slightly lower thermal stability of HBPBO-3/Epoxy as compared to HBPBO-1/Epoxy and HBPBO-2/Epoxy was attributed to the nonstoichiometric curing of epoxy because of the large amount of o-aminophenol groups in HBPBO-3.

The surface wetabilities of epoxy and composites were also evaluated by contact angle (CA) analysis (Figure 9). Epoxy showed CA of 94.1°, indicating its slightly hydrophobic nature. However, it is found that the addition of different HBPBOs caused opposite effect on the CA of epoxy. The addition of HBPBO-1 and HBPBO-2 increased the CA to 104.9° and 106.1°, respectively. While the addition of HBPBO-3 changed the surface of epoxy to slightly hydrophilic with CA of 87.6°. The increased CA in HBPBO-1/Epoxy and HBPBO-2/Epoxy was attributed to the introduction of fluorine atoms in the systems. While the decreased CA in HBPBO-3/Epoxy were also attributed to the

Table II. The Thermal and Mechanical Properties of Epoxy and HBPBOs/Epoxy Composites

	T_5 (°C)	T_d (°C)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation to break (%)
Epoxy	395.5	411.0	1.78 ± 0.17	69.7 ± 5.2	7.61 ± 1.14
HBPBO-1/Epoxy	411.1	420.2	1.87 ± 0.09	63.9 ± 2.4	6.16 ± 0.14
HBPBO-2/Epoxy	407.2	419.5	1.76 ± 0.08	71.7 ± 3.5	7.90 ± 0.43
HBPBO-3/Epoxy	405.8	416.7	1.74 ± 0.06	59.8 ± 7.3	6.53 ± 0.28

nonstoichiometric curing of HBPBO-3/epoxy, which left higher amount of hydrophilic –OH and –NH$_2$ groups on the surface. Such phenomenon was in consistent with the lower thermal stability of HBPBO-3/Epoxy as revealed by TGA analysis. The increased hydrophobic of epoxy upon the addition of HBPBO-1 and HBPBO-2 is helpful for the utilization of epoxy in applications in microelectronics, because them could lower the absorption of moisture.[35]

The mechanical properties of composites were also investigated by tensile testing, the results were listed in Table II. The results suggested that the mechanical properties of epoxy were not influenced too much by the addition of HBPBOs, because of the low addition amount of HBPBOs in epoxy and both the HBPBOs and epoxy were with 3D cross-linked structures.

CONCLUSIONS

We have reported a one-pot A$_2$+B$_3$ strategy for the synthesis of soluble hyperbranched PBO with 6FAP and BTA as A$_2$ and B$_3$ monomers. Controlled experiments suggested that the highly branched structure of HBPBOs and flexible hexafluoropropane groups in the branched backbone both contributed to the good solubility of HBPBOs in organic solvents. The branched structure was proved to distort the coplanarity of rigid rod-like PBO chains, thus prevented the chains from tight packing, which was helpful to exploit their optical properties. TGA measurements indicated the characteristic high thermal stability of PBO was not obviously deteriorated by the introduction of branched structure. Because of the good solubility of HBPBOs, we also fabricated the molecular composites of HBPBOs and epoxy resins. The incorporation of small amount HBPBOs have demonstrated to improve the thermal stability and alter the surface wettability, while maintain the mechanical integration of epoxy resins. The results presented here were expected to provide hints for the design of novel hyperbranched aromatic polymers and composites.

AUTHOR CONTRIBUTIONS

Jing Wu contributed in the experimental operation, acquisition and analysis of data, and preparation of the manuscript. Yan Wang contributed in the experimental design, analysis and interpretation of data, and revision of manuscript. Junrong Yu contributed in the analysis of data and revision of manuscript. Jing Zhu contributed in the interpretation of data. Zuming Hu contributed in the experimental design and interpretation of data.

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